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**PURIFICATION, GROWTH AND CHARACTERIZATION
OF $Zn_xCd_{1-x}Se$ CRYSTALS**

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ABSTRACT

We report here on the purification of starting materials which were used in growth of $Zn_xCd_{1-x}Se$ ($x=0.2$) single crystals using the traveling solution method (TSM). Up to 13 cm long single crystals and as grown resistivities of 6×10^{12} ohm.cm could be achieved. Infrared and Raman spectra of $Zn_{0.2}Cd_{0.8}Se$ are also presented and discussed.

$6 \times 10^{12} (exp 12)$

unreported

PURIFICATION, GROWTH AND CHARACTERIZATION OF $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ CRYSTALS

Introduction

The existence of the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ single crystal system was demonstrated as early as 1951 (1) and its potential for optoelectronic applications is due to the possibility of obtaining variable energy gaps from 1.74 to 2.67 eV. The materials are interesting as phosphors for color TV applications (2) and, more recently, the lasing properties of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ single crystals, for $x=0.33$, were reported (3).

Growth of medium resistivity crystals of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ has been demonstrated in the past using the temperature gradient solution zoning (TGSZ) method (4). Following this development, $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ has been proposed (5) as an alternate material to CdSe for room temperature nuclear radiation detection because replacement of Cd by Zn in the crystal lattice results in an increased energy band gap and a higher resistivity material, which is a prerequisite for such an application. Crystal growth using the traveling solution method (TSM) was successfully applied to the growth of tellurides (6,7), resulting in low contamination and good crystalline perfection. It was therefore interesting to determine the possibilities of this method in the case of selenides, which involve higher growth temperature and pressure.

In this paper we present the steps completed in our research program, which include: the purification of raw materials; the crystal growth using the traveling solution method (TSM), which, to the best of our knowledge, is the first attempt to use this technique for the growth of selenide crystals; and the characterization of the as-grown crystals by electric measurements and by Raman and infrared spectroscopy.

Experimental

a) Purification. CdSe commercial reagents (Alfa, 99.999% purity on a metal basis, and General Electric, electronic grade) were subjected to repeated vacuum sublimations at 700 and 1000°C. Unlike Cd and Zn, Se is not commercially available in high enough purity and therefore we used Se of 99.999% purity (Johnson Matthey) which was further purified in a laboratory built zone refiner.

b) Crystal growth. Up to 40 g of raw material composed of Zn and Cd having 99.9999% purity (Cominco), in the desired composition, together with a stoichiometric amount of Se of 99.999% purity (Johnson Matthey) were loaded in a quartz reaction ampule. The ampule was vacuum sealed at 10^{-5} torr, mounted in a laboratory designed and built rocking furnace, and then the temperature was increased slowly (100°C/day) up to 900°C. After two weeks the reaction was completed and the charge was used as starting material, together with 10% additional Se, in the crystal growth experiment. The crystal growth ampule had an internal diameter of 1 cm and was 26 cm long. The crystal growth system included a three zone furnace mounted on a vertical translational stage. The middle zone was narrow, (approx. 5 cm) with the highest temperature slowly (10°C/min) increasing to 1170°C, while the upper and lower zones were kept at 970°C. The ampule was static and the furnace was moved upwards at 0.5 to 2 cm/day.

c) Characterization. Samples were prepared by cleaving the crystal along the a or c planes, followed by grinding and polishing to the desired thickness. Lapping and etching were performed in a solution containing 10% bromine in methanol. Electric contacts were applied using aquadag paint or by vacuum evaporation of Au. A SPEX Model 1403 Double Spectrometer and a Coherent Model Innova 90 Ar laser (514.5 nm, 800 mW) were used to record the Raman spectra. The Fourier transform infrared spectra were recorded in the 400- 4000 cm^{-1} range using a Bomem DA.3 FT-IR spectrometer.

Results and Discussion

The diffuse reflectance infrared Fourier transform (DRIFT) spectra of the raw material, CdSe powder purchased from two different vendors, have shown the presence of peaks which can be assigned to the sulphate group. The reaction of CdSO_4 with H_2Se is one common way to synthesize CdSe, and the presence of an unreacted residue of CdSO_4 could be the explanation for these impurity bands. DRIFT spectra of repeated vacuum sublimed powders showed that the SO_4^{2-} bands disappeared, due probably to thermal decomposition. However, the method was probably not sufficiently efficient in removing the sulphur impurity. CdSe crystals grown using this purification method have shown a new band appearing at 540 cm^{-1} , which was attributed to sulphur impurity induced modes (8). We have therefore used the synthesis from Zn, Cd and Se elements as preparation of the starting material for crystal growth using TSM. Up to 13 cm long single crystals could be grown using the above technique. Fig. 1 shows an infrared transmittance spectrum obtained from a 0.5 mm thick sample. The absence of any major band around 540 cm^{-1} proves that synthesis from elements results in $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ crystals having less S impurity. We did not observe a broad band, such as the one seen in the 500 to 1200 cm^{-1} region in Bridgman grown CdSe (8), which was attributed to infrared absorption by free carriers in non-stoichiometric (Cd-rich), low resistivity crystals. The I-V curve of an as-grown $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{Se}$ sample is shown in Fig. 2. From the slope of the graph we can calculate a resistivity of 6×10^{12} ohm.cm, which is the highest reported for this class of ternary compounds (4).

The vibrational properties of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ were studied using Raman scattering and the spectra are shown in Fig. 3. The general features agree with a previous study (9) where crystals were in the $x=0.4$ to 1 composition range. From Valakh et al. (9) spectra and from our spectra it can be concluded that $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ belongs to the one-mode type of crystals in which the frequency of the LO-phonon changes continuously versus crystal composition.

More work is under way to calibrate these LO frequencies against actual composition as determined by chemical analysis, which will enable us to use Raman measurements for determinations of Zn/Cd molar ratio distributions along the crystalline boule.

Acknowledgment

The research was sponsored by NASA, Grant no. NAG8-113.

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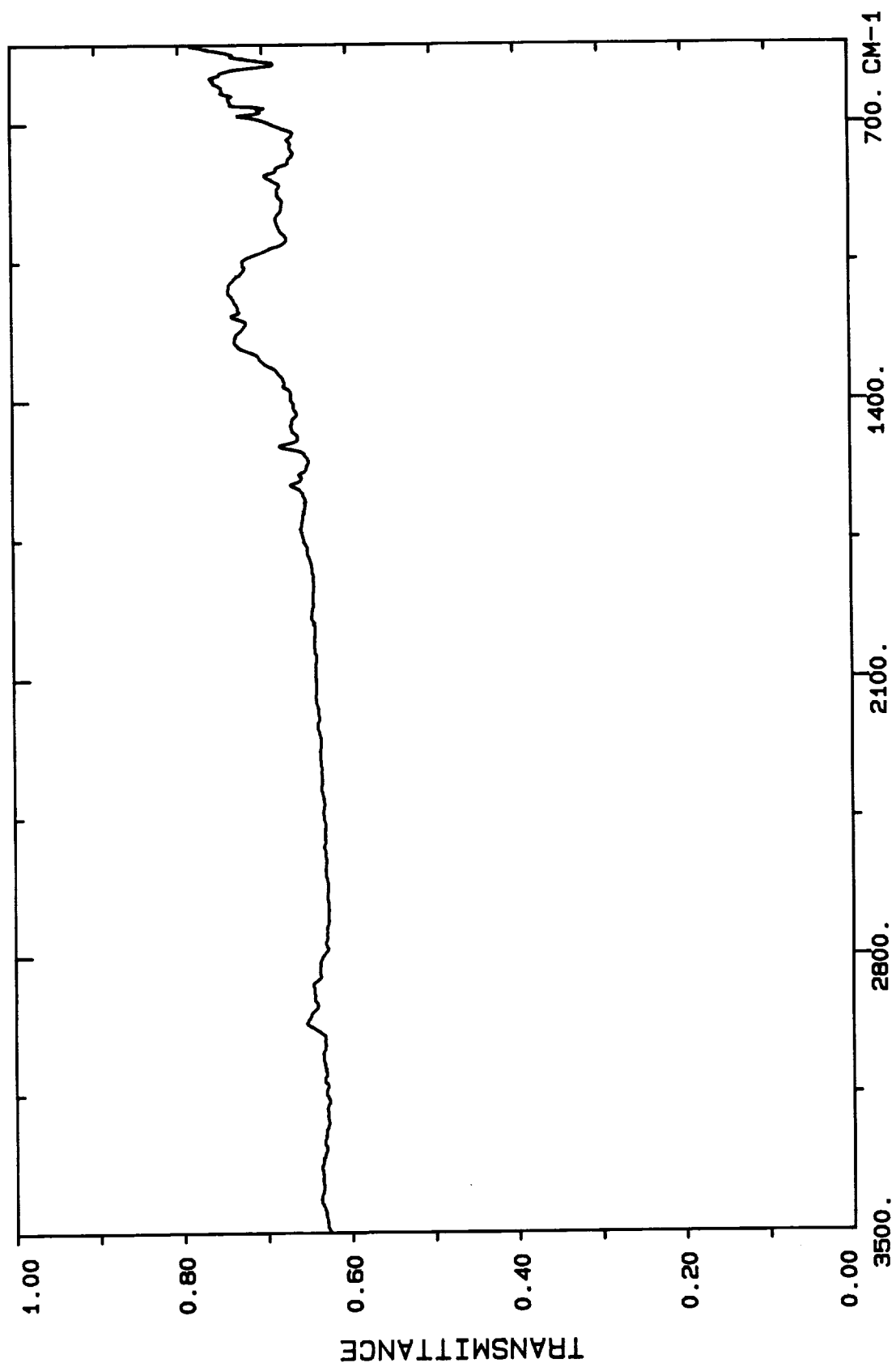


Figure 1.
Infrared transmittance spectrum from a 0.5 mm thick $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{Se}$ single crystal.

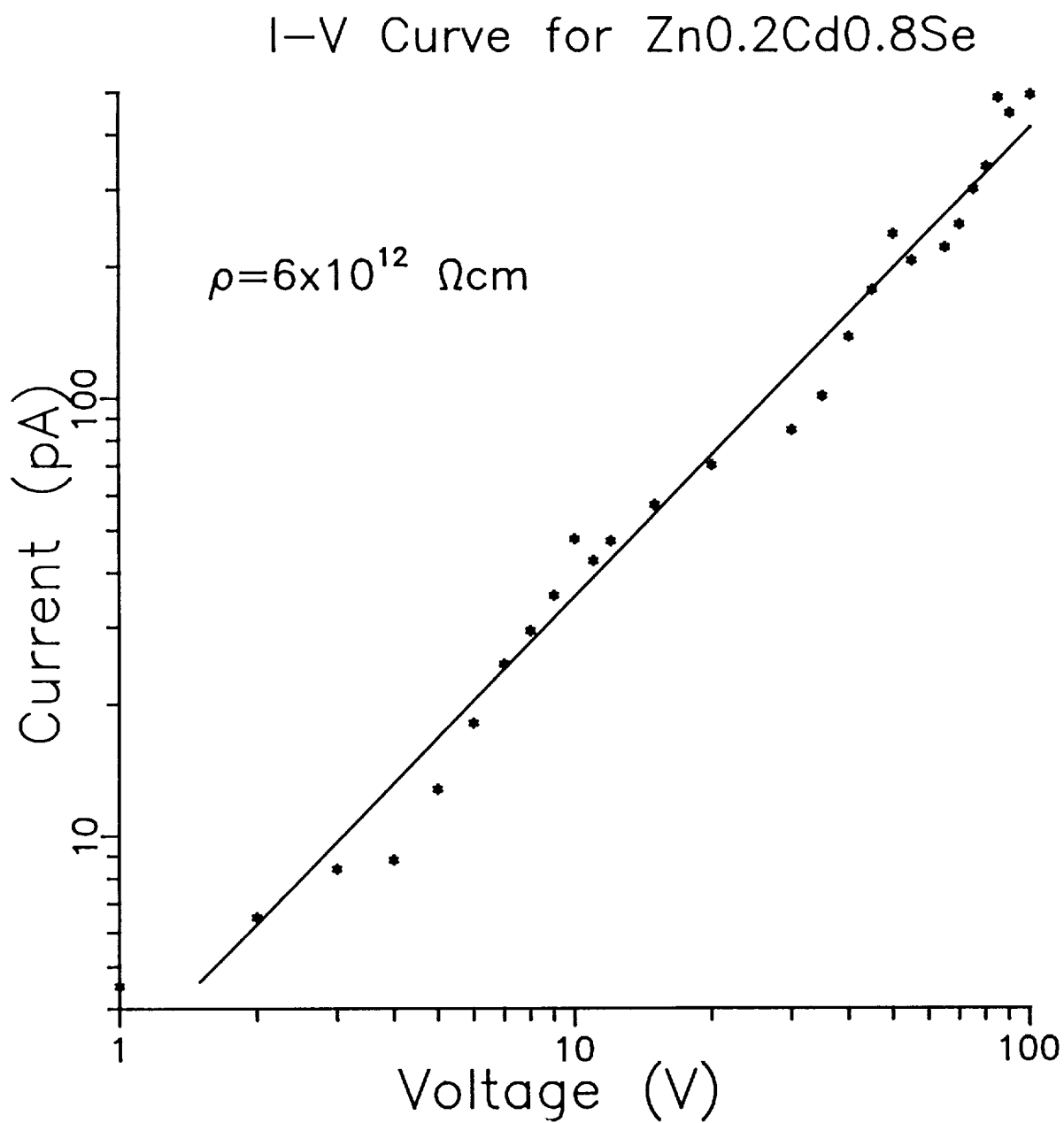


Figure 2.
The I-V curve of an as-grown $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{Se}$ sample, 0.15 cm thick, 0.06 cm² contact area.

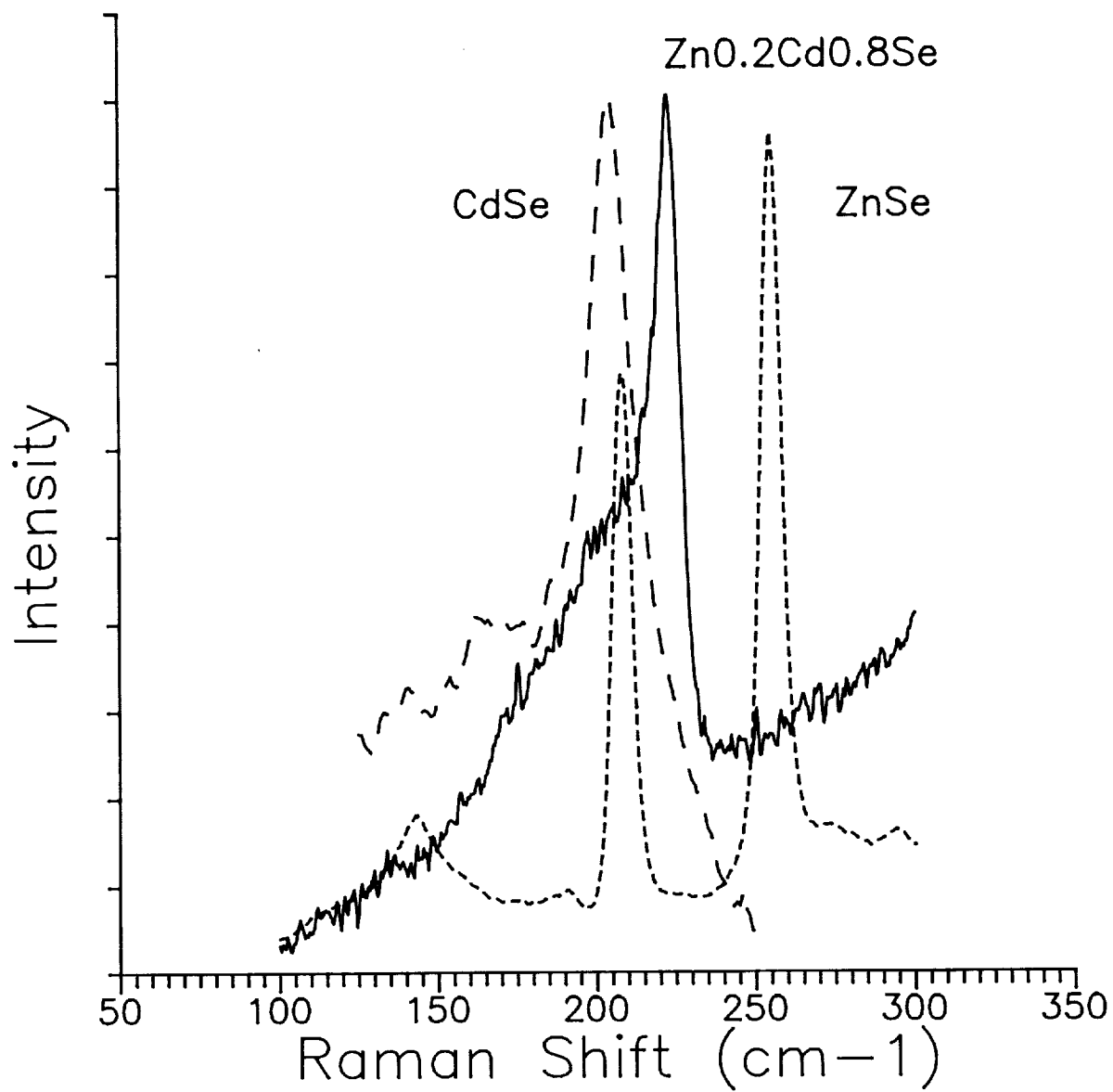


Figure 3.
Raman scattering spectra for CdSe , $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{Se}$ and ZnSe single crystals.